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Scaling of the energy for multiply charged two electron systems by a perturbative procedure

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Abstract : A Z-perturbative procedure is used to obtain simple algebraic relations between the total energies of two electron diatomic systems belonging to the same sequence in the aim of their utilisation in scattering problems. As a direct application, values of the total energy of He_2^{3+} and Li_2^{4+} are obtained from those of H_2 and H_2^+. The method reproduces well the pseudo-crossing locations of the considered diatomic systems.

Keywords : Total energy for multiply charged diatomic systems, Z-perturbative procedure.

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1. Introduction

Diatomic systems, having the same nuclear charge ratio Z_a/Z_b, and the same number of electrons, could be classified like atomic systems in sequences. The Born-Oppenheimer solutions, for the ions belonging to the same sequence, present similarities, which have been only scarcely used for the one electron (Bates *et al* 1953, Helfrich and Hartman 1970, Power 1973, Wilson and Gallup 1966) and many electron (Marcias 1979) sequences. With the growing interest in multiply charged diatomic ions in the intermediate and Miraglia 1989 and low energy (Ponomarev and Puzynina 1967, Erea *et al* 1985, Olson and Salop 1977) scattering studies, and with the general tendency to classify in a periodic table different types of molecules, it becomes useful to exploit these similarities, which not only permit to avoid unnecessary calculations, but offer a better understanding of the physical situation and Miraglia 1989.

Recently we have pointed out (Joulakian 1988a) the possibility of deducing B.O. wave functions, and thus, spectroscopic properties for one electron sequences, from existing ones. Then we have deduced (Joulakian 1988b) approximate values of the total energy for two electron systems (atomic and

diatomic) without any integration by establishing simple relations between existing accurate energy values of two other members of the same sequence.

The aim of this paper is to show that, when calculating the total energies of non-degenerate states of a given two electron system, energy values of all the members of the corresponding sequence can be deduced by simple algebraic relations. It is true, that nowadays, calculations, on this type of diatomic systems, are considerably facilitated by performing computers, but such similarities and relations are still very useful for workers who need rapid results. More they could be extended to many electron diatomic systems. And finally, they permit a better understanding of the common properties of such systems.

2. Method

Following the Lennard-Jones-Brillouin-Wigner (LBW) procedure (Dalgarno 1961, Luke *et al* 1969) we express the total energy of non-degenerate states of two electron diatomic system (Z_a, Z_b, R), where R is the internuclear distance, in the form

$$E_i(R) = E_i^{(0)}(R) + E_i^{(1)}(R) + E_i^{(2)}(R) + Z_a Z_b / R, \tag{1}$$

where the zero order energy is $E_i^0(R) = \epsilon_{ui} + \epsilon_{vi}$ (2)

with ϵ_{ui} and ϵ_{vi} being the monoelectronic energies.

The first order term $E_i^{(1)}(R) = I_{ii} + \Pi J_{ii}$ (3)

and the second order term $E_i^{(2)}(R) = \sum_{j \neq i} \frac{(I_{ij} + \Pi J_{ij})^2}{E_i^0 - E_j^0}$ (4)

with $I_{ij} = \langle u_i(r_1) u_i(r_1) \mid r_{12}^{-1} \mid v_i(r_2) v_i(r_2) \rangle$ (5)

and $J_{ij} = \langle u_i(r_1) v_j(r_1) \mid r_{12}^{-1} \mid u_j(r_2) v_i(r_2) \rangle$ (6)

$\Pi = -1$, 1 for triplet and singulet states respectively, and $\Pi = 0$ for the cases where $u_i = v_i$. u_i and v_i being the corresponding diatomic orbitals, exact solutions of the one electron two centre Schrödinger equation, eq. (11).

Let us consider two two-electron diatomic systems in the same state satisfying the relation

$$\sigma = Z'_a / Z_b = Z'_b / Z_b = R / R' \tag{7}$$

Rewriting eq. (1) for a second (primed) system we have

$$E'_i(R') = E_i^{0\prime}(R') + E_i^{(1)\prime}(R') + E_i^{(2)\prime}(R') + Z'_a Z'_b / R' \tag{8}$$

Using the relations $E_i^{0\prime}(R') = \sigma^2 E_i^0(R)$

$$E_i^{(1)\prime}(R') = \sigma E_i^{(1)}(R)$$

and $E_i^{(2)\prime}(R') = E_i^{(2)}(R)$,

and by eliminating the second order terms between eq. (1) and eq. (8), we obtain

$$E'_i(R') = E_i(R) + (\sigma^2 - 1)E_i^0(R) + (\sigma - 1)E_i^{(1)}(R) + (\sigma^3 - 1)Z_a Z_b/R \qquad (9)$$

This relation, gives the total energy $E'_i(R')$ of a non-degenerate state of a given two electron diatomic system in terms of the supposedly known value $E_i(R)$ of another member of the same sequence. $E_i^0(R)$ and $E_i^1(R)$ are also supposed to be known, as they enter in the determination of $E_i(R)$.

3. Calculations

In the following, we present some immediate applications of eq. (9) to the two-electron diatomic homonuclear sequence (H_2, He_2^{2+}, Li_2^{4+},...) using the known values of H_2 and H_2^+. Our aim is not to give extensive tables, but to show, by comparing our values to the existing ones, the validity our approach.

For the He_2^{2+}, $\sigma' = 2$ and eq. (9) becomes

$$E'_i(R/2) = E_i(R) + 3E_i^0(R) + E_i^{(1)}(R) + 7/R \qquad (10)$$

Here $E_i(R)$ is the corresponding H_2 total energy, which are available in other publications (Kolos *et al* 1986).

$E_1^0(R)$, that of H_2^+, which we determined together with the $E_i^1(R)$ using symmetrized Slater type diatomic orbitals (Bishop and Cheung 1983, Wells and Wilson 1986) expressed in prolate spheroidal coordinates λ, μ, ϕ ($1 \leqslant \lambda \leqslant \infty$, $-1 \leqslant \mu \leqslant 1$, $0 \leqslant \phi \leqslant 2\pi$), which are solutions of the two centre Schrödinger equation.

$$U_a(r_a, r_b, m, R) = \{(\lambda^2 - 1)(1 - \mu^2)\}^{m/2} \exp(im\theta)\phi(r_a, r_b, R) \qquad (11a)$$

$$\phi(r_a, r_b, R) = \sum_i \exp(-\alpha_i \lambda) \sum_j \lambda_j \sum_k C_{ijk} \mu^k (\exp(-\beta_i \mu) + (-1)^{q+k} \exp(\beta_i \mu)) \qquad (11b)$$

here $q = m$ or $q = m + 1$ for *gerade* and *ungerade* states respectively.

The use of this type of symmetrized one electron solutions in the calculation of two electron integrals brings out some important simplifications.

In Table energy values for the lowest state $(1s\sigma_g)^2 \Sigma_g$ of He_2^{2+} are given in the range $R = 0.8$ to 3 a.u. and compared to the accurate values of Yagisawa *et al* (1977) using the corresponding H_2 values of Kolos *et al* (1986). The accuracy varies between 0.1% to 0.4%, which is very satisfactory considering the small computational effort required.

Table I. Total energies of He_2^{3+} and Li_2^{4+} (column 4 and 5) deduced from those of H_2 (column 2). (a) Kolos et *al* (1986). (b) Yagisawa et *al* (1977) (in a.u.).

	Known values			Deduced values	
		$(1s\sigma_g)^2\ ^1\Sigma_g$			
R	$1s\sigma_g H_2^+$	$H_2\ X\Sigma_g$ (a)	He_2^{3+} (b)		Li_2^{4+}
0.8	1.55448009	1.020056598	0.642899	0.64000	−4.6940
1.0	1.45178631	1.124539660	1.948626	1.94520	0.1332
1.2	1.36230786	1.164935191	2.677649	2.67365	2.9588
1.4	1.28426924	1.174475668	3.103879	3.09921	4.7131
1.6	1.21593724	1.168583330	3.358481	3.35305	5.8459
1.8	1.15580920	1.155068695	3.510705	3.50440	6.5969
2.0	1.10263422	1.138132913	3.599729	3.59241	7.1033
2.2	1.05538508	1.120132069	3.648961	3.64040	7.4485
2.4	1.01337135	1.102422553	3.672960	3.66394	7.6871
2.6	0.97544858	1.085791176	3.681096	3.66942	7.8466
2.8	0.94149886	1.071683159	3.679574	3.66572	7.9570
3.0	0.91089620	1.057326175	3.672587	3.65589	8.0320

In Table 2 values of the total energy for the states $(1s\sigma_g 2p\sigma_u)\ ^1\Sigma_u$ and $^3\Sigma_u$ are given between $R=1$ to 9 a.u. and compared to those given by Yagisawa et *al* (1977) using the corresponding values of Kolos and Wolniewicz (1966, 1968).

The satisfactory results obtained above permits us to apply the same procedure to other excited states of He_2^{2+} like non-degenerate levels $(1s\sigma_g 2p\pi_u)\ ^1\pi_u$ and $^3\pi_u$, for which no results exists to the best of our knowledge. These values have been obtained using the corresponding values given by Kolos and Rychlewski (1976, 1977).

Once the values of the total energy for He_2^{4+} are determined, and the accuracy of the results tested, the total energy of another member of the homonuclear sequence Li_2^{4+} can be given rightaway from eq. (9), which becomes for $\sigma'=3$

$$E'_i(R/3)=E_i(R)+8E_i^{(0)}(R)+2E_i^{(1)}(R)+26/R \tag{12}$$

It should be emphasized here that the $E_i^1(R)$ has already been calculated for He_2^{2+} and that generally we need not calculate them as they should be determined in $E_i(R)$.

Results are presented in Tables 1, 2 and 3 for the states $X\Sigma_g\ ^1\Sigma_u\ ^3\Sigma_u\ ^1\pi_u$ and $^3\pi_u$ respectively.

We can remark that as the nuclear charges increase, the domain of R reduces. This does not present a major difficulty, moreover, it is a confirmation of the fact

Table 2. Total energies of the states $^1\Sigma_u$ and $^3\Sigma_u$ of He_2^{3+} and Li_2^{4+} deduced from those of H_2. (a) Kolos and Wolniewicz (1966), (b) Yagisawa *et al* (1977), (c) Kolos and Wolniewicz (1968) (in a.u.).

		Known values		Deduced values		Known values		Deduced values	
			$^3\Sigma_u$				$^1\Sigma_u$		
R	$2p\sigma_u$ H_2^-	H_2 (a)	He_2^{3+} (b)	He_2^{3+}	Li_2^{4+}	H_2 (c)	He_2^{3+} (b)	He_2^{3+}	Li_2^{4+}
1.0	0.56481364	0.6125227	−0.784698	−0.7897	−8.0065	0.5812963	−0.987633	−0.9930	−8.3818
2.0	0.66753439	0.8970636	2.306840	2.3073	3.4431	0.7520541	1.861723	1.8702	2.7140
3.0	0.70141830	0.9720104	3.152498	3.1522	6.5403	0.7524996	2.586769	2.5879	6.6870
4.0	0.69555064	0.9933781	3.459471	3.4591	7.7083	0.7354677	2.823956	2.8194	7.1486
5.0	0.67729161	0.9986849	3.593600	3.5938	8.2665	0.7147955	2.898526	2.9132	7.5576
6.0	0.65731056	0.9998125	3.668588	3.6674	8.5995	0.6948364	2.915515	2.9132	7.3962
7.0	0.63912886	1.0000030	3.709587	3.7157	8.8314	0.6772076	2.912056	2.9174	7.5576
8.0	0.62360602	1.0000196	3.737896	3.7510	9.0059	0.6623056	2.898994	2.9054	7.6767
9.0	0.61065494	1.0000127	3.751768	3.7644	9.1425	0.6500475	2.882364	2.9173	7.7701

Table 3. Total energies of the states $^1\pi_u$ and $^3\pi_u$ of He_2^{++} and Li_2^{4+} deduced from those of H_2. (a) Kolos and Rychlewski (1977), (b) Kolos and Rychlewski (1976) (in a.u.).

	Known values	Deduced values			Known values	Deduced values	
		$^1\pi_u$			$^3\pi_u$		
R	$2p\pi_u$ H_2^+	H_2	He_2^{++}	Li_2^{4+}	H_2	He_2^{++}	Li_2^{4+}
1.0	0.47410796	0.57250622	0.1210	9.3764	0.58846014	- 1.1939	- 8.8843
2.0	0.42877182	0.71823825	1.4207	0.7015	0.73747639	1.4657	0.7723
3.0	0.38644385	0.68926739	1.9153	3.0452	0.70747743	1.9441	3.0848
4.0	0.35082464	0.65667247	2.0581	3.8998	0.67142579	2.0782	3.9253
5.0	0.32138481	0.63707918	2.1186	4.3094	0.64736928	2.1318	4.3256
6.0	0.29699156	0.62844255	2.1587	4.5569	0.63481122	2.1667	4.5665
7.0	0.27663158	0.62548781	2.1908	4.7300	0.62932052	2.1955	4.7356
8.0	0.25951063	0.62467509	2.2859	4.7207	0.62708857	2.2887	4.7238
9.0	0.24502514	0.62453544	2.2361	4.9590	0.62615333	2.2334	4.9612

that the multicharged systems arrive very rapidly to their separated atom distances, beyond which, the total energy has a constant value.

4. Conclusion

We have shown that the energy values for multiply charged two electron systems could be obtained from those of a member of the same sequence. The simplicity of the method together with its relatively well precision, makes it a very useful method in scattering problems, the extension of which to multielectron systems could now be foreseen.

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